

DEVELOPMENT OF HIGH TEMPERATURE MEMBRANES AND IMPROVED CATHODE CATALYSTS

Project Period: January 1, 2002 – December 31, 2005

Recipient: UTC Fuel Cells

Prime DOE Contract Number: # DE-FC04-02AL67608

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Objectives

- Develop and demonstrate advanced high concentration platinum cathode catalysts that will enable the reduction of Pt loading according to the DoE's technical targets and meet DOE's goals for performance.
- Develop and demonstrate ion-exchange membranes capable of operating at 100°C and 25%RH. Understand the issues connected to the operation of PEM fuel cell in the temperature range of 100-120°C and reduced RH%. Understand the impact of operating conditions on advanced polymeric membrane, catalyst, catalyst support, etc.

Approach

Current project consisted of three main phases and eighteen milestones. Short description of each phase is given below. Table 1 lists program milestones.

- Phase 1. *High Temperature Membrane and Advanced Catalyst Development.* New polymers and advanced cathode catalysts were synthesized. The membranes and the catalysts were characterized and compared against specifications that are based on DOE program requirements. The best-in-class membranes and catalysts were down-selected for phase 2.
- Phase 2. *Catalyst Coated Membrane (CCM) Fabrication and Testing.* Laboratory scale catalyst coated membranes (CCMs) were fabricated and tested using the down-selected membranes and catalysts. The catalysts and high temperature membrane CCMs were tested and optimized.
- Phase 3. *Multi-cell stack fabrication.* Full-size CCMs with the down-selected and optimized high temperature membrane and catalyst were fabricated. The catalyst membrane assemblies were tested in full size cells and multi-cell stack.

PHASE	MILESTONE #	MILESTONE
Phase 1 Membrane Chemistry and Catalyst Development	1	Preliminary model completed
	2	Begin alloy synthesis
	3	Complete alloy synthesis
	4	Complete characterization and down-selection
	5	Complete modeling + correlation
	6	Membrane specification to team members
	7	Initial sample membrane
	8	Characterization of initial membrane samples
	9	Synthesis of final membrane samples
	10	Select membrane for Phase 2
Phase 2 MEA Development and Testing	11	Initial electrode fabrication
	12	Complete subscale testing for cathode catalyst and down-select catalysts
	13	Complete subscale testing for membranes and down-select membrane(s)
	14	Select optimum catalyst-membrane combination for Phase 3
Phase 3 Stack Demonstration and High Temperature Fundamentals	15	Complete stack and test stand assembly
	16	Complete stack verification test
	17	Fuel cell demonstration of the best performing high temperature materials
	18	Fuel cell demonstration of performance and durability best MEA materials for HT operation

Table 1 Program Milestones

Highlights of Program Achievements

- Established the importance of cycling durability
- Developed best in class PtIrCo alloy catalyst and demonstrated 5x cyclic durability improvement vs. Pt
- Established membrane down-select criteria
- Demonstrated impact of high temperature and reduced RH on membrane durability
- Developed fundamental understanding of hydrocarbon membrane durability
- Demonstrated 1000 hours operation at 100°C, 25%RH

Motivation

Polymer Electrolyte Membranes (PEMs) currently available for fuel cell development work are limited to the temperature range of 60-80°C. For mass commercialization in the transportation arena, three important disadvantages that are linked with the relatively low operating temperature range need to be addressed. These three disadvantages are: (a) sluggish cathode kinetics, (b) CO poisoning at the anode and (c) inefficient thermal characteristics. All three of the above mentioned disadvantages could be solved by increasing the operating temperature range to 100-120°C.

To understand the issues associated with high temperature PEMFCs operation, UTCFC has teamed with leading research groups that possess competencies in the field of polymer chemistry. The subcontractors on the program were investigating modified Nafion® and new non-Nafion® based, reinforced and non-reinforced membrane systems. Nafion® based PEMs rely on using high temperature inorganic solid conductor fillers like phosphotungstic acid. Hydrocarbon membrane systems are based on poly (arylene ether sulfone) polymers, PEEK, PAN, etc.

Due to complexity and lack of understanding of the issues that one might face operating PEM FCs at 100-120°C and reduced RH%, UTC FC initiated a fundamental research to investigate RH and high temperature impact on membrane and electrodes degradation.

For the commercialization of PEM fuel cells, it is also imperative to reduce cost and improve the power density. At the CCM level, cost and power density are linked through the loading of Pt metal used to overcome the enormous activation overpotential for the Oxygen Reduction Reaction (ORR). In order to improve performance with reduced Pt loading, it is necessary to develop new and higher activity Pt catalyst systems. In order to achieve the aggressive DoE target of cell performance higher activity catalyst layers need to be used in conjunction with reduced thickness such that even a mass transport benefit is realized.

Results and Discussion

High Temperature Fundamentals and Membrane Development

Phase 1.

Material Development.

To develop high temperature PEMs, UTCFC has teamed with research groups that possess competencies in the field of polymer chemistry and engineering. The subcontractors on the program are investigating modified Nafion[®] and new non-Nafion[®] based membrane systems. The new non-Nafion[®] membrane systems include Poly(arylene ether sulfone), acidified and sulfonated PBI, PEEK, PAN, etc. Nafion[®] based PEMs rely on using high temperature inorganic solid conductor fillers like zirconium phosphate.

The sub-contractors on the program are VA Tech, IONOMEM/UCONN, Penn State University, Princeton and Stanford Research Institute (SRI). Details of the approaches taken by the sub-contractors are briefly summarized in Table 2

Group	Principal Investigator	Approach
IONOMEM/UCONN	Mr. Leonard Bonville, Dr. James Fenton	Hygroscopic solid ion conductor (e.g., zirconium phosphate, etc) filled Nafion [®])
Penn State University	Prof. Digby Macdonald	Sulfones and sulfoxides of aromatic PPBP and aliphatic PVA. Covalent sulfonic acid bonded PEEK, PBI and PPBP
Princeton University	Prof. Andrew Bocarsly	Layered sulfonated Polystyrene/Fluoropolymer system
Stanford Research Institute	Dr. Susanna Ventura	Sulfonated PEEK-PBI-PAN
Virginia Tech	Prof. James McGrath	Sulfonated Poly(arylene ether sulfone)

Table 2. High Temperature Membrane Program Approach

First two years of the program were dedicated to material development and development of techniques for ex-situ materials screening. As interim target, UTC FC has stressed the importance of the conductivity requirements for HTMs at 120°C and 50% RH. Results

were compared to Nafion[®] 112. Phase 1 was concluded in March 2004 by down-selection process.

Down-Select Results

Five different membranes were subjected to ex-situ tests that included conductivity, water uptake, mechanical/structural strength, dimensional changes. All the measurements were conducted under elevated temperature, low humidity or after the membranes were subjected to these conditions for a set period of time. The emphasis was set on conductivity values. Figure 1(A) shows the area specific resistivities of the various membranes as calculated from the thickness and the 4-electrode conductivity measurements. The target data point for the study is 120°C, 50% RH. At this point, only the IONOMEM/UCONN membrane approached the cut-off target imposed in the program. No other membrane, reached this resistivity target except at RH values exceeding 70 %.

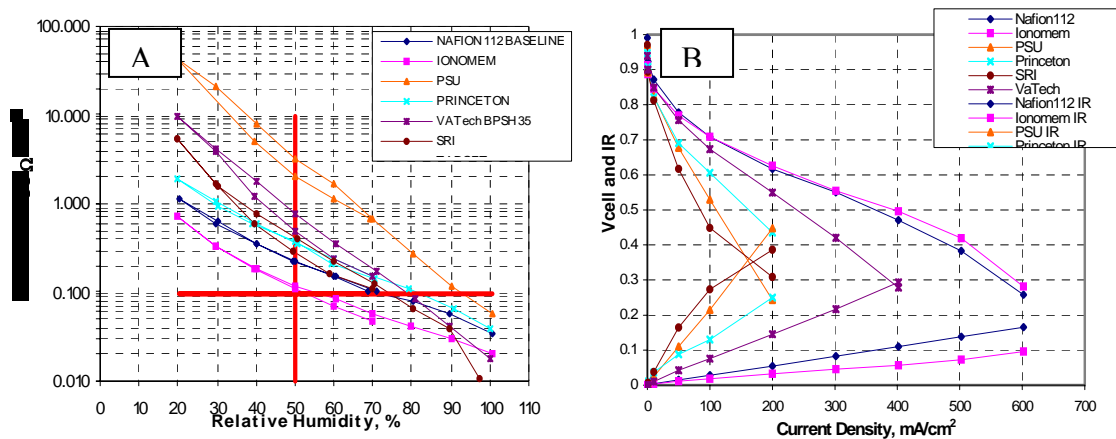


Figure 1. (A) Area specific resistivity ($\Omega \text{ cm}^2$) of the various subcontractor's membranes compared to Nafion[®].baseline; (B) Fuel cell performance: 120°C, 50%RH, 150 kPa (abs), H₂/Air, U:30%/ 25%.

All the membranes were also tested in fuel cells at 120°C and 50%RH for performance evaluation. Figure 1(B) shows the peak performance of the various subcontractor membranes at 120 °C and 50 %RH. Under these conditions, the inlet oxygen

concentration at 150 kPa was roughly 10.5 %. Results clearly show that UCONN's performance is significantly greater than the other subcontractor's under these conditions. In all cases, performance differences in the membranes are predominantly due to the difference in membrane conductivity. At UTCFC, each membrane was dry-pressed at 130°C between two catalyzed Toray GDLs. The electrodes contained Nafion[®] ionomer and a catalyst loading of 0.4 mgPt/cm² on the anode and cathode. The UEAs were then conditioned at 80°C and 75%RH before raising the operating temperature to 120°C, 50% RH.

The membranes were ranked based on results of tests (see Table 3) and two best membranes were selected for Phase 2 of the program. UCONN's membrane was selected for CCM optimization and VATech was chosen to work on further membrane properties improvement and fundamental studies of hydrocarbon-type membrane in application for PEM FCs.

Criteria	Criteria Subcategory	Weight	Ranking (1 to 5, 5 = highest, 0 = failure)					
			Nafion [®]	Ionomem	VaTech	Princeton	SRI	PSU
Conductivity – 50 % Total	20% RH*	0.125	3	4	1	2	1	1
	50% RH*	0.25	3	4	2	2	2	1
	100% RH*	0.125	3	3	4	3	4	3
Water Uptake - 20% Total	40 % RH Vapor	0.15	3	3	1	2	2	2
	Liquid	0.05	3	2	5	1	1	1
Performance – 30 % Total	IR BOL	0.1	3	4	3	2	1	2
	IR EOL	0.1	3	4	3	1	0	0
	crossover EOL	0.1	3	1	3	3	0	0
SCORE = $\Sigma(\text{Weight} * \text{Ranking})$			3.0	3.325	2.425	2.075	1.575	1.3

Table 3. Results of the Down-Select Tests in HTM program.

Phase 2.

Majority of the work in this phase is dedicated to the CCM optimization and durability studies of the down-selected material. In addition, VATech, whose material showed promising results but performed worse than established baselines, was selected to further work on material properties improvement and for fundamental studies toward understanding of hydrocarbon membrane durability in fuel cell conditions.

UCONN's Membrane CCM Optimization

The UCONN's technical approach for high temperature PEM catalyzed membranes integrates, on a molecular level, the proton-conducting Nafion[®] polymer with hygroscopic solid proton conductors such as phosphotungstic acid. This innovative nanocomposite material maintains low water vapor pressure, provides more water-independent proton conduction, and holds promise of satisfying DOE performance requirements.

Several CCM optimization approaches were looked at, with priority on optimization of the ionomer content, catalyst and porosity of the cathode. A modeling effort in parallel with experimental work was put into the understanding of the trends of the impact that various CCM changes can have on cell performance (See Figure 2).

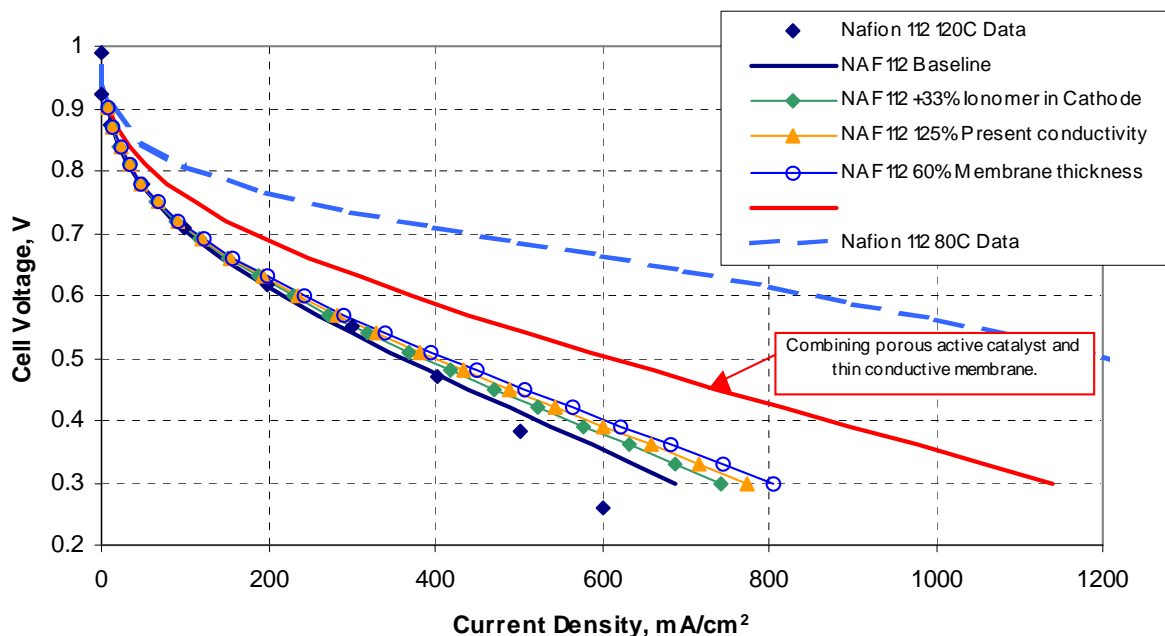


Figure 2. Simulation of Nafion® 112 Cell Performance at 120 C, 0 hours 50% RH, 150 kPa (abs), s based on Bekktech data. Utilizations not taken into account

As was mentioned above, some of the experimental optimization steps included ionomer content optimization and ionomer equivalent weight optimization (Figure 3).

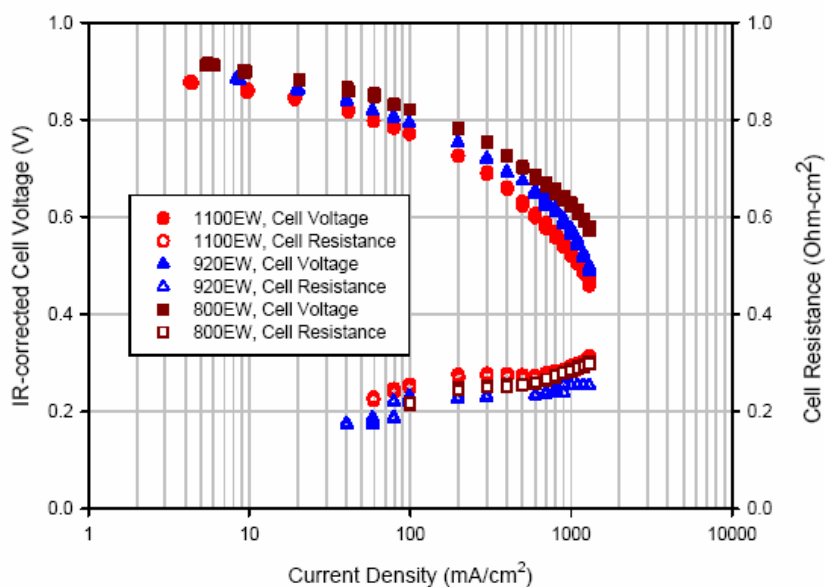


Figure 3. Effect of the ionomer equivalent weight on the cell performance. Test conditions: 120°C, 35%RH, 1atm, H₂/O₂

Optimization of ionomer content in electrodes resulted in the optimum value of 28%. This content is optimum for both high temperature and low RH operating conditions and for fully humidified lower temperature operation.

Phase 3.

Scope of work in Phase 3 was related to demonstration of durability of down-selected UCONN's membrane and its scale up to full size fuel cell platform. Significant effort was also placed into understanding of high temperature durability of PFSA-like and hydrocarbon membrane. Hydrocarbon membrane from VATech was developed and studied through the time period of Phase 1 - Phase 3. For the purpose of continuous story flow all the results on hydrocarbon membrane research will be summarized in this section.

Durability of UCONN's PFSA PTA-doped membrane

A new membrane formulation designated as Series IV has been developed in UCONN after the down-select process. The fabrication process of this formulation is significantly different from the down-selected Series II membrane and was targeted toward improvement of membrane durability. Phosphotungstic acid (PTA) particles are precipitated in situ, resulting in much smaller particle size. The PTA is added in Cs form, and the resulting membrane is now processed in the Cs form allowing for higher processing temperatures ($>180^{\circ}\text{C}$), resulting in greater crystallinity (+durability) of the membrane as well as providing insoluble form of PTA and thus eliminating leaching of PTA particles during 100% RH operation.

A 1000-hour Series IV membrane endurance test was run on 25cm^2 fuel cell. Both the anode and cathode catalysts were $0.4\text{mgPt}/\text{cm}^2$ of TTK 46.7% Pt/C containing 32% Nafion®. The operating conditions were $400\text{ mA}/\text{cm}^2$, 100°C and 25% RH for both the H_2 and air reactants. The cell was maintained as a constant current with cell performance and resistance recorded. Periodic crossover, ECAs and cell polarization curves were used as diagnostic tools for the cell. Result of this endurance test is shown in Figure 4 and 5.

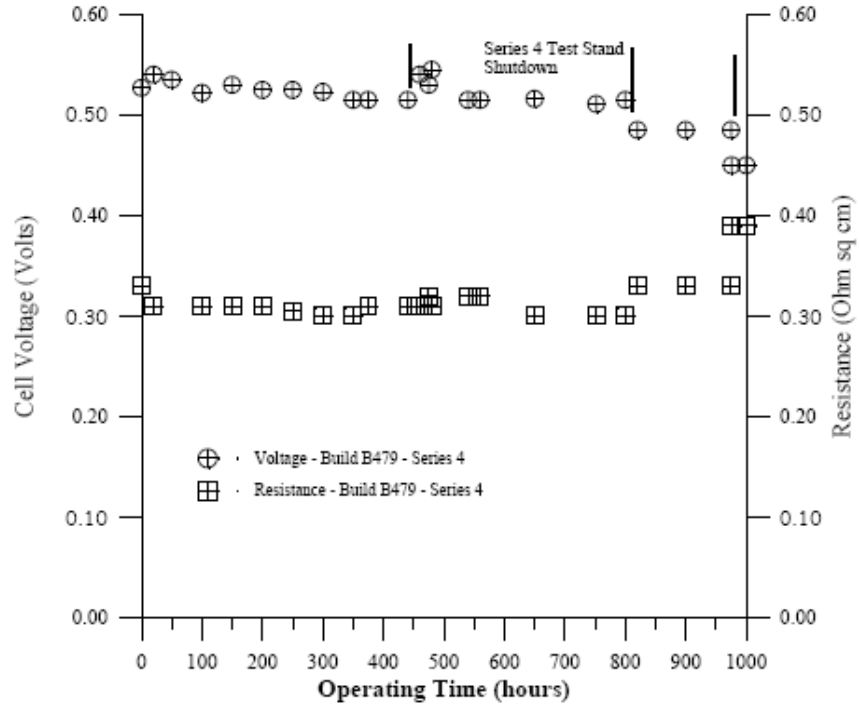


Figure 4. Performance and resistance history of UCONN Series IV endurance cell.

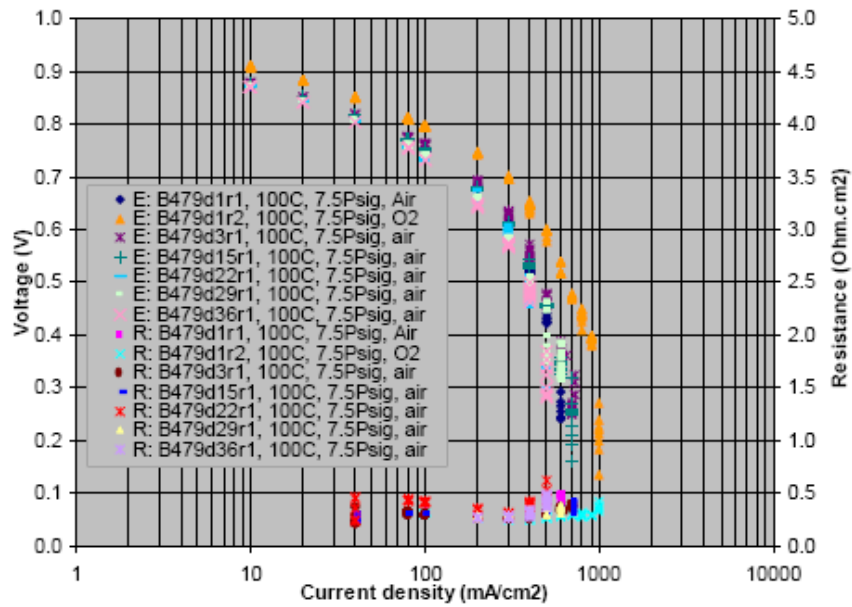


Figure 5. Polarization curves for UCONN Series IV cell during endurance test.

The decay in the cell performance was due to some deterioration of the cathode structure (concluded from electrochemical area (ECA) changes) and slight change in membrane resistance. Membrane crossover during the duration of the test did not increase (see Figure 6).

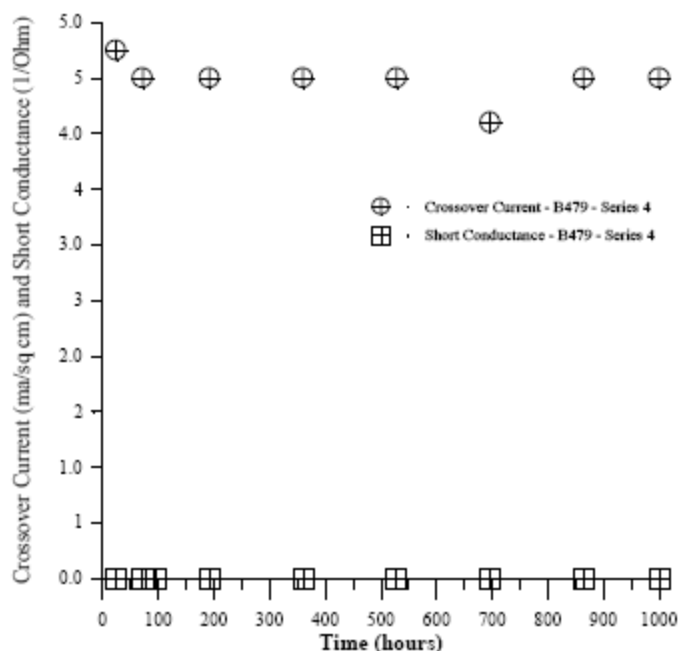


Figure 6. Crossover and shorting data for UCONN S4 endurance test.

High Temperature Fundamentals

High temperature fundamentals research was carried out in two parallel steps: durability studies of the effects of accelerating conditions using subscale single cells and performance studies as full size single cell work in combination with theoretical modeling. This work was done using PFSA membrane.

PFSA Performance at High Temperature

In order to establish effect of temperature and relative humidity on the performance of Nafion[®]-like membranes, a series of performance curves were then run over a temperature range of 80 – 120 C, a relative humidity range of 25 – 50 % RH, and a

utilization range of 25 – 80% H₂, 25 – 60% Air, and 5 – 60% O₂. Results are summarized in Figure 7.

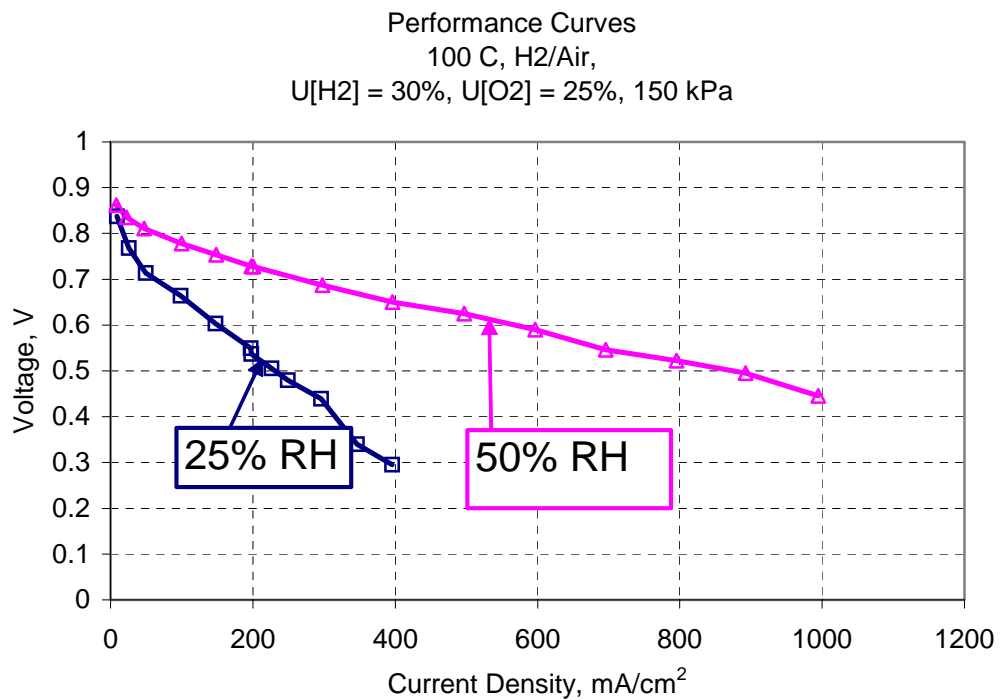
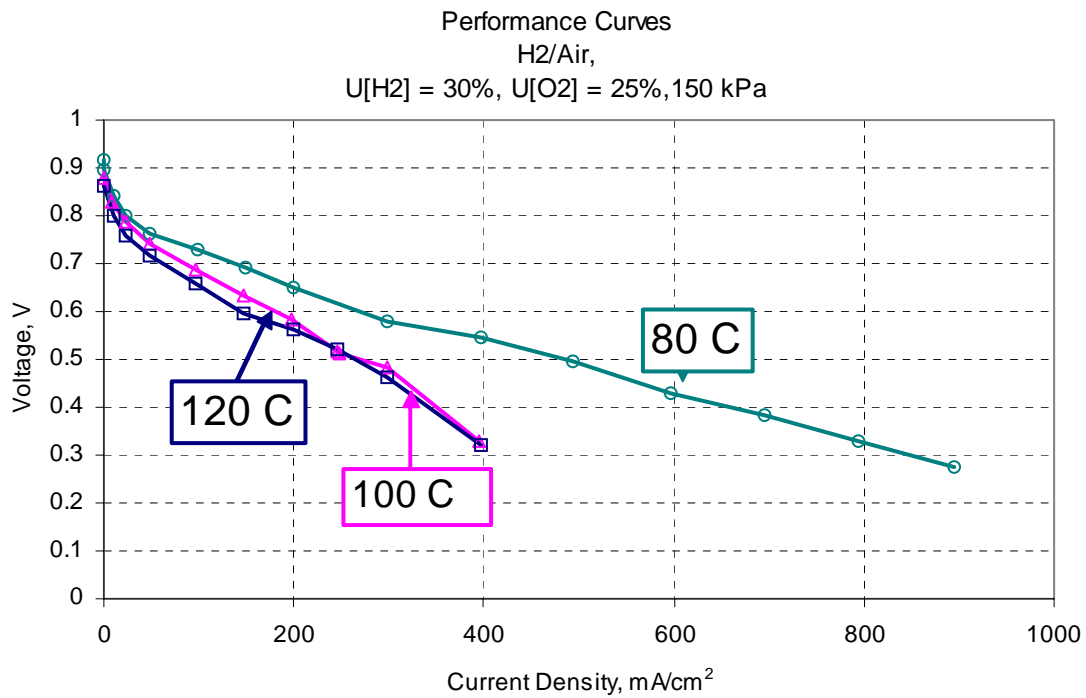


Figure 7. The effect of temperature and pressure on cell performance.

Perhaps the most significant effect is that of utilization on performance for low relative humidities as shown in Figure 8. Running on higher utilization improves performance due to higher water content of the membrane vs. lower utilization. These experimental results are in a good agreement with theoretical predictions (see Figure 9).

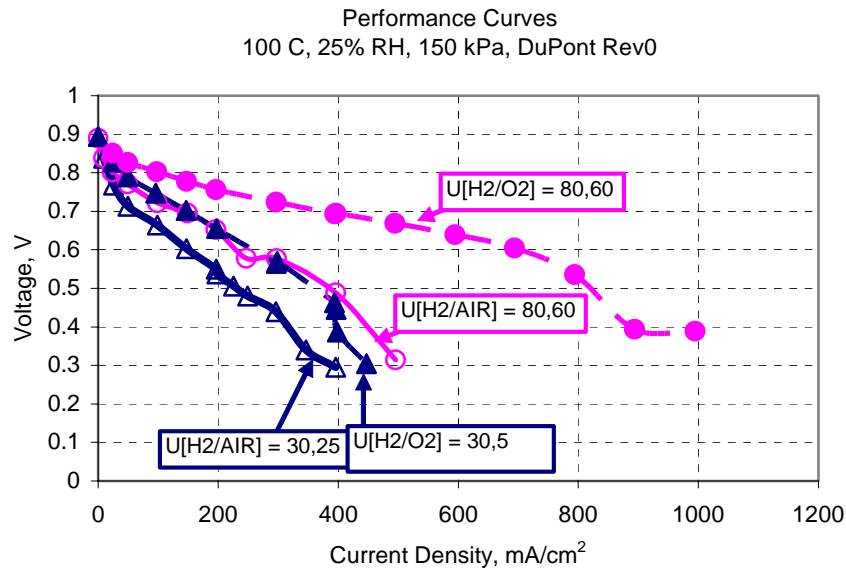


Figure 8. The effect of utilization on performance at the DoE design point of 100 C, 25% RH.

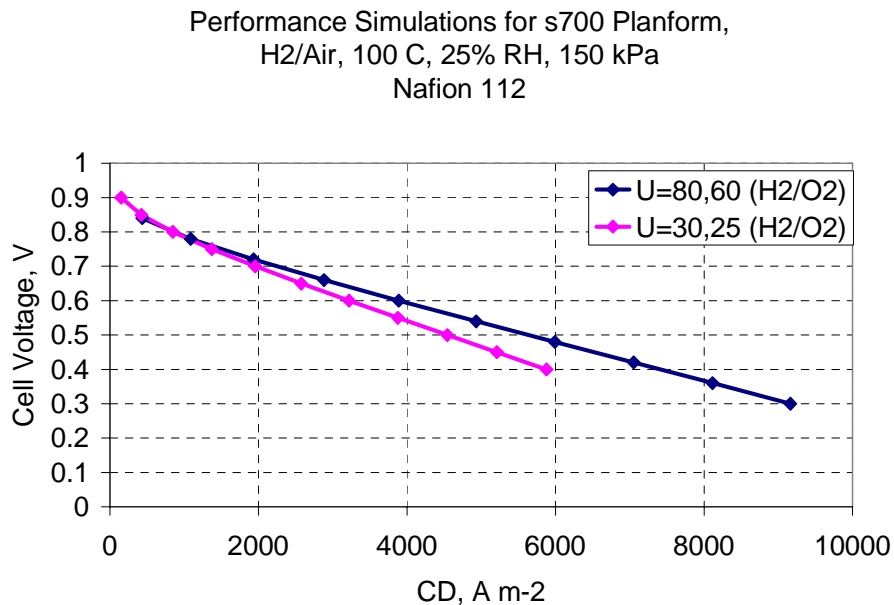


Figure 9. Nafion® 112 100C and 25%RH simulated performance

These observations are also consistent with theoretical modeling that shows that at dry conditions relative humidity (and thus - conductivity of membrane) is the key factor that determines current density distribution in fuel cell (see Figure 10). This is in contrary to the conventional operating conditions (100% RH) where current density profile is set by oxygen concentration.

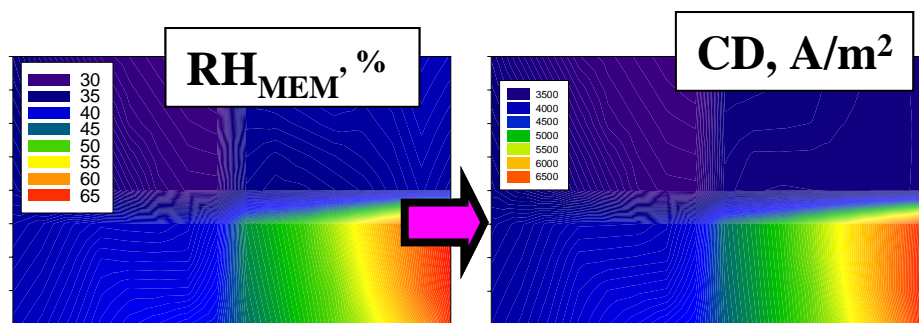


Figure 10. Modeling results to demonstrate effect of membrane conductivity (dependant on RH%) on current density distribution in fuel cell.

PFSA Durability at HT Fuel Cells

Accelerated OCV decay tests were used in these studies to identify acceleration factors of high temperature and low RH operation. Identical composition MEAs were tested at temperature of 80, 100 and 120°C in the 25-75%RH range. Hydrogen crossover was used to monitor membrane degradation. Results of these tests are summarized in Figures 11 and 12. It has been shown that temperature has much stronger impact on FERs than relative humidity. This can be explained by strong dependence of O₂ permeability through membrane on temperature. Electrochemical monitoring technique has been developed in UTC FC to determine oxygen permeability through membrane at various temperatures and RHs. Nafion[®] permeability was found to increase with temperature and decrease with relative humidity. At the same time at constant temperature only week dependence of O₂ permeability on relative humidity was obtained. This observation is consistent with in-cell membrane tests. In case of reduced relative humidity effect, the membrane failure is accelerated by degradation of mechanical properties of PFSA. In dry

conditions the membrane becomes mechanically brittle and can not tolerate large fluoride loss.

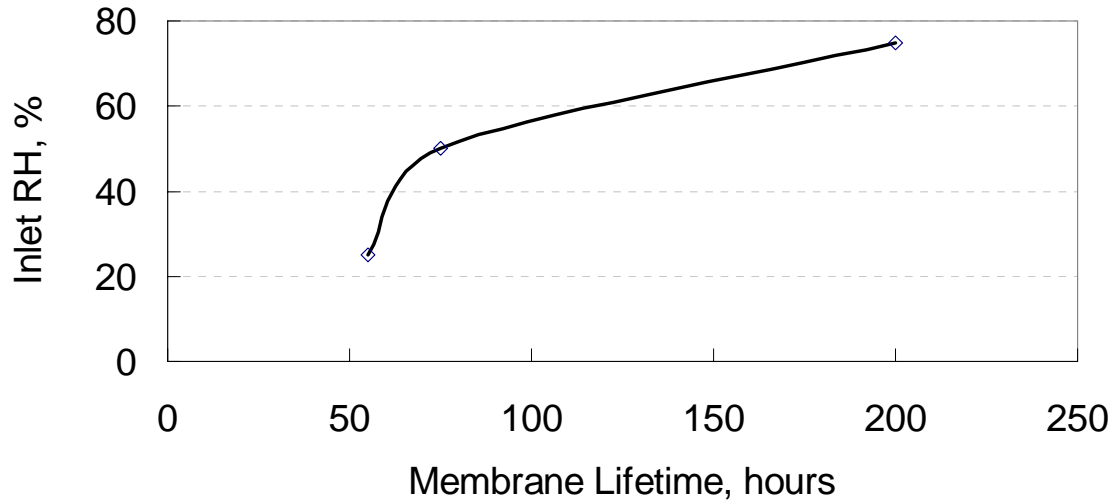


Figure 11. Effect of humidity on Nafion[®] 112 degradation at OCV decay test. Test conditions: $p[\text{O}_2]=96\text{kPa}$ for all trials; 100°C , H_2/O_2 , 150kPa .

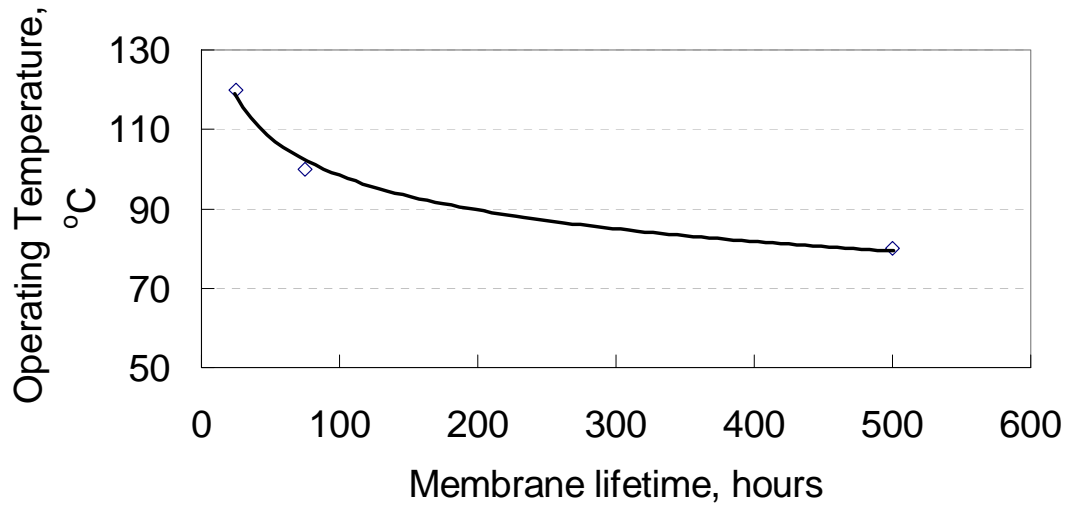


Figure 12. Effect of temperature on Nafion[®] 112 degradation at OCV decay test. Test conditions: $p[\text{O}_2]=96\text{kPa}$ for all trials; $25\%\text{RH}$, H_2/O_2 , 150kPa .

Hydrocarbon Membrane Development and Fundamentals

Hydrocarbon membrane developed in VATEch was based on the approach of the direct copolymerization of wholly aromatic poly(arylene ether sulfone) sulfonic acid copolymers and to optimize compositions for PEM applications. The resulting proton conducting materials are hypothesized to have sufficient resistance to acidic conditions, to withstand hydrolysis during the fuel cell process, and also to resist actual concentrations of the proposed hydroxyl radicals formed during the oxygen reduction.

Aromatic ionomers are copolymers that are comprised largely of repeating thermally stable aromatic rings, which are stiffer, stronger, have higher glass transition temperatures than Nafion[®] and yet can be designed to produce ductile films. They are quite thermally and oxidatively stable. The acidity is somewhat lower than the Nafion[®] fluorosulfuric acid, which may be an important parameter in fuel cells at low relative humidities. The aromatic random ion-containing copolymers, such as illustrated in Figure 1 can be generated either via a post reaction or direct copolymerization processes.

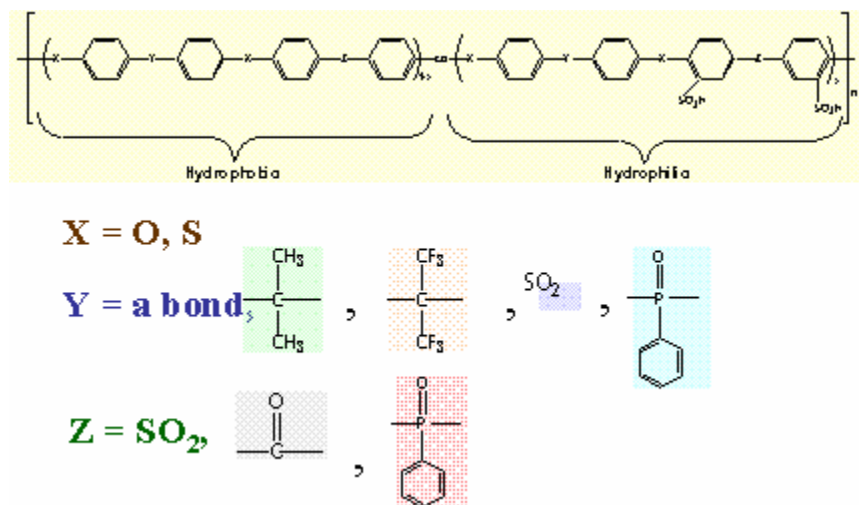


Figure 13. Wholly aromatic random copolymer proton exchange membranes developed in VATEch

VaTech's group have shown that the direct copolymerization process has many advantages, such as enhanced stability, control of the ion-containing sites, a wide variety of molecular structures, the ability to make higher molecular weights, which transforms into tougher, more durable films. Long block sequences are also feasible. The direct copolymerization involves first generating an ion-containing monomer, which allows one to modify the basic characteristics of the films from hydrophobic to hydrophilic¹. The 4,4'-biphenol based poly(arylene ether sulfone) copolymers have been most extensively studied and have developed the acronym BPSH-xx, to represent biphenol sulfone in the acid form. The XX represents the molar fraction of sulfonic acid units in the copolymer repeat unit. Thus, "BPSH-35" would have 35% units containing sulfonic acid moieties.²

Several accelerated membrane degradation tests were run to evaluate durability of BPSH membrane. Those included so-called Fenton test, OCV degradation test, potential/load cycling, and relative humidity cycling tests.

Currently Fenton test is being widely accepted for ex-situ evaluation of proton exchange membrane chemical stability. Fenton test results on BPSH showed that this membrane fully deteriorates during the time when Nafion® losses only 15% of its weight (Figure 14). Further discussion explains how Fenton results can be misleading if used for evaluation of hydrocarbon membranes and prediction of their durability in PEM FCs.

¹ Sankir, et al, *J. Appl. Poly Sci.*, 2005, in press

² F. Wang, *J. Mem Sci.*, 2002

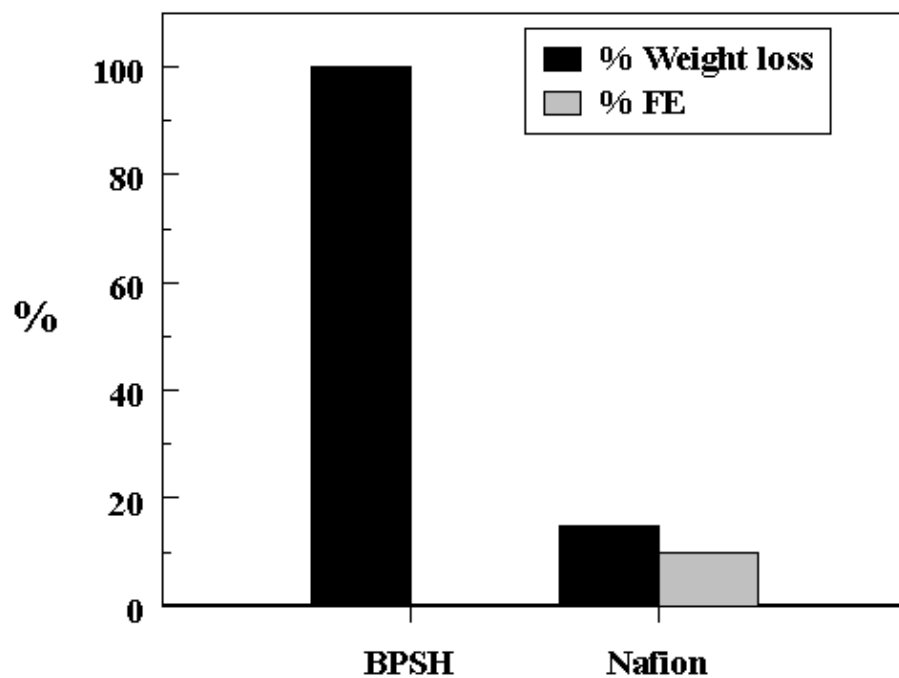


Figure 14. Results of Fenton test on Nafion and BPSH membranes.

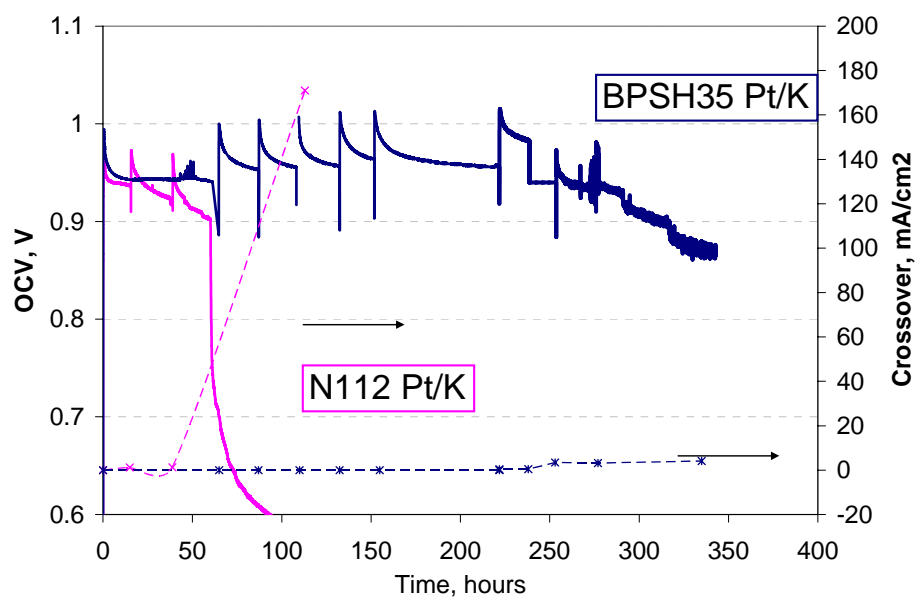


Figure 15. Results of OCV hold membrane test on BPSH and Nafion 112. Test conditions: 120°C, 25%RH, H₂/O₂

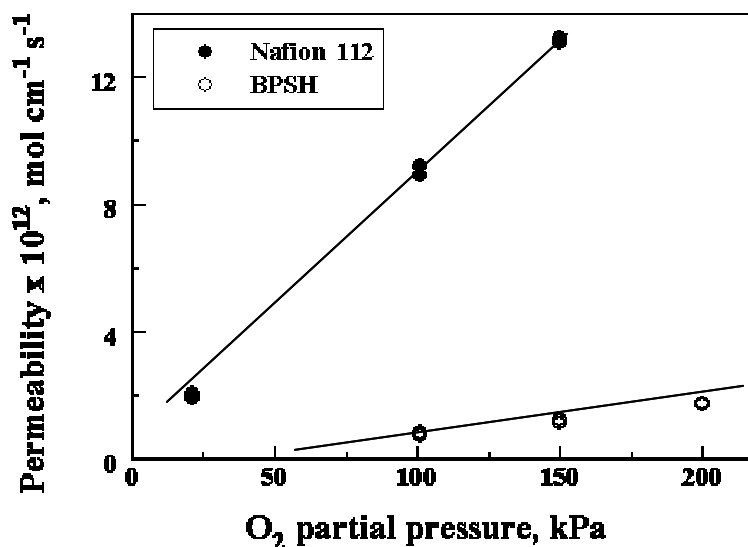


Figure 16. Oxygen permeability through Nafion and BPSH membranes.

Figure 15 demonstrates that BPSH membrane significantly outlives Nafion membrane in accelerated open circuit voltage (OCV) hold fuel cell test. This long membrane life can be explained by extremely low oxygen permeability through such hydrocarbon membranes (see Figure 17). This fact is completely overlooked in Fenton test, which puts all membranes in equally harsh chemical conditions.

The BPSH membrane has also outlived Nafion® 112 membrane during cycling test at 100°C (see Figure 17). Durability protocol for this test has included potential cycling on H₂/O₂ between 1V and 0.38V and subsequent OCV hold at 100°C and 25%RH. Post test SEM images showed that Nafion® membrane had thinned significantly, while the thickness of BPSH membrane stayed intact (Figure 18).

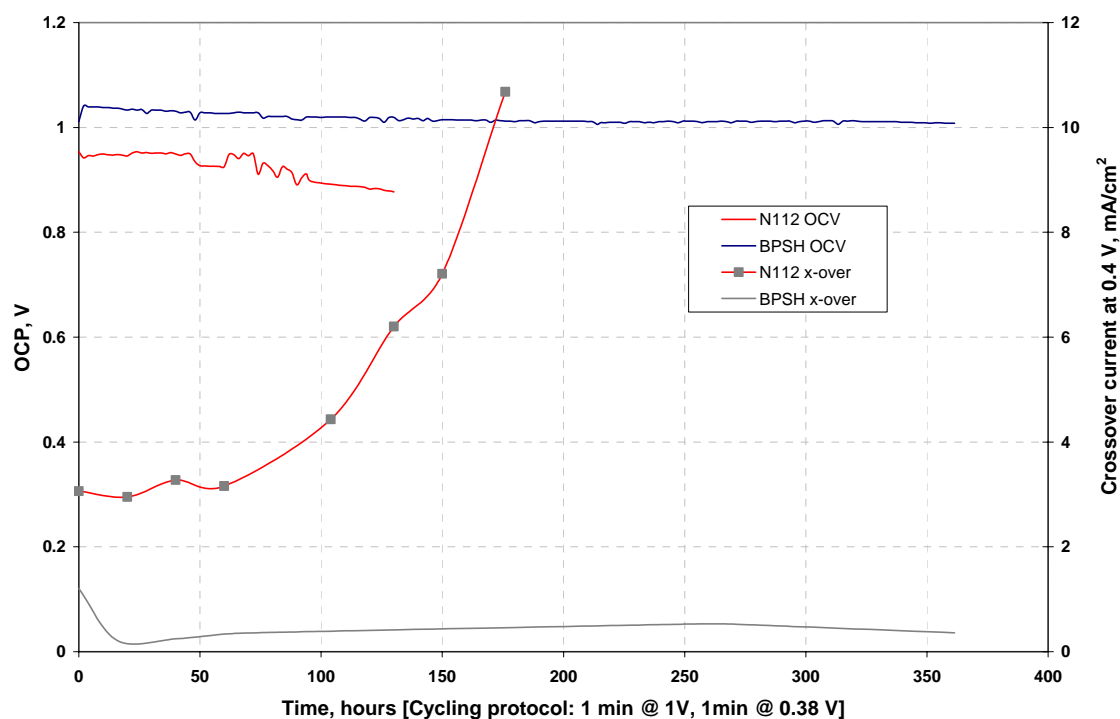


Figure 17. Cycling Results for BPSH and Nafion® 112 cells: OCP Decay & Hydrogen Cross-over Current. Test conditions: 100 C, 25% RH, 150 kPa, 0.5SLM H₂ [Anode], 1.0 SLM O₂ [Cathode]

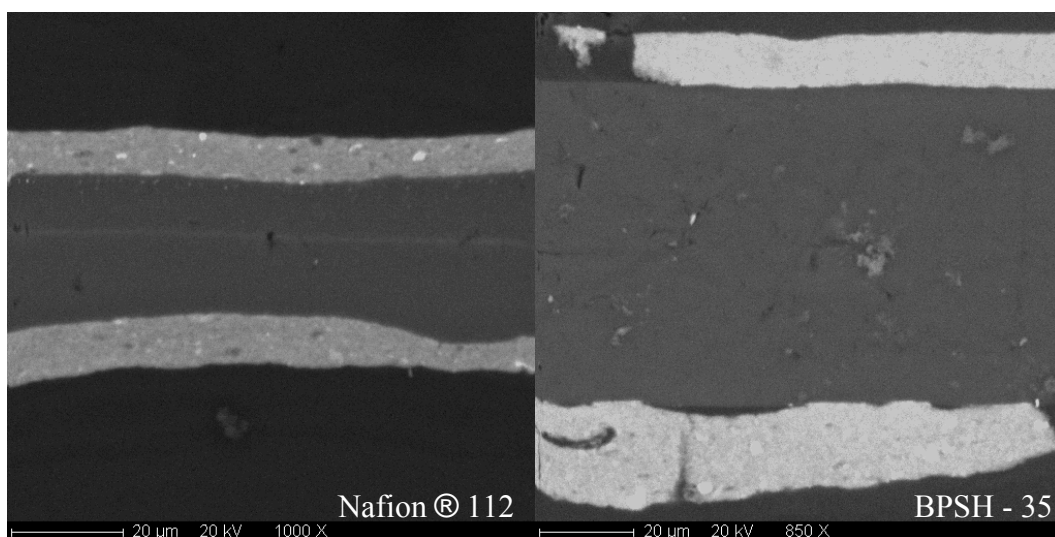


Figure 18. SEM results of cross-sectioned Nafion® 112 and BPSH membranes that undergone potential cycling on H₂/O₂. Original thickness of BPSH was 70µm.

At the same time most hydrocarbon membranes exhibit large linear expansion upon hydration. This behavior can lead to premature failure of the MEA during relative humidity (RH) cycles in realistic fuel cell systems. UTC FC conducted a series of tests to determine extend of swelling and linear expansion of BPSH-35 during hydration. The membrane was boiled in water for 1 hour and change in x-y-z direction was recorded and compared to Nafion[®] films. Results of these tests are summarized in Table 4. Mechanical stability of this membrane toward RH cycling (0-100%RH) at 100°C was also investigated *in-situ*. Nafion[®] 112 passed 200 hours test, while BPSH failed mechanically after ~25 hours. Results of these tests are shown in Figure 19..

Membrane	Linear expansion x-direction, %	Linear expansion y-direction, %	Swelling (boiling), %
BPSH-35	25	15	41.2
Nafion [®] 112	10	3.1	11.4

Table 4. Dimensional Stability of BPSH-35

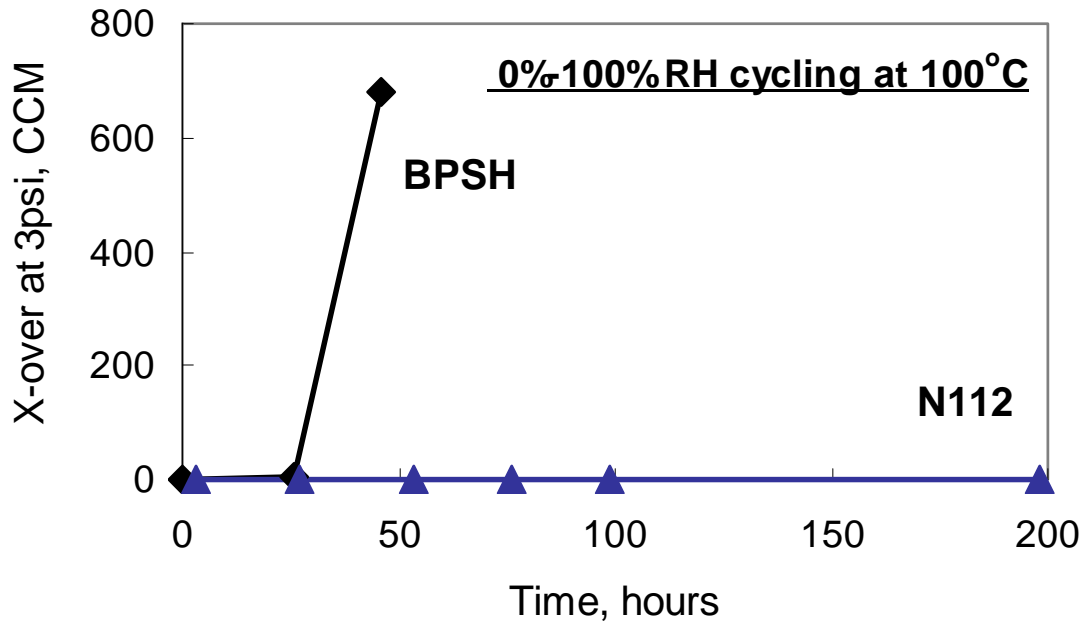


Figure 19. Results of RH% cycling tests on BPSH-type membrane.

Such dimensional instability of BPSH membrane prevents from its successful implementation in fuel cell MEAs. Figure 20 shows that large cracks developed in MEA during GDL unitizing procedures due to significant expansion and contraction of the BPSH.

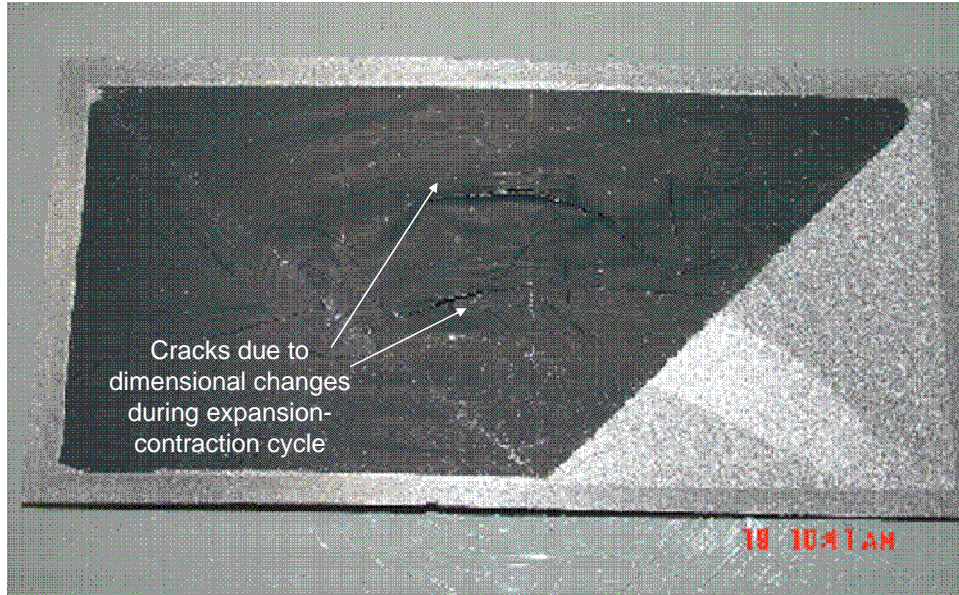


Figure 20. BPSH MEA after unitizing procedure with gas diffusion layer.

Cathode Catalyst Development

Phase 1.

Synthesis Approaches

Under Cathode Catalyst Development part of the project, first two years were dedicated to material development and development of techniques for ex-situ screening and modeling work. The subcontractors involved in the catalyst program and their individual approaches is given in Table 5. The synthesis techniques and the catalyst systems that will be synthesized by the three groups are also outlined in Table 5.

Group	Principal Investigator	Approach
North Eastern University (NEU)	Prof. Sanjeev Mukerjee	Micellar Pt nano cluster synthesis, colloidal sol synthesis of binary Pt alloys.
University of South Carolina (USC)	Prof. Branko Popov	Pulse electro-deposition of Pt and Pt alloys on Carbon. [Pt and Pt-X, X=Fe, Ni, Co, Mn and Cu]
UTC Fuel Cells (UTCFC)	Dr. Lesia Protsailo	Carbothermal synthesis of ternary Pt alloys. [Pt-Ir-X and Pt-Rh-X, [X =Ni, Co and V]]
Case Western Reserve University (CWRU)	Prof. Al Anderson	Quantum chemical modeling of Pt alloys and ORR.
UT Research Center (UTRC)	Dr. Ned Cipollini	Reproducible and stack size CCM fabrication.

Table 5. Advanced Cathode Catalyst Program Approach

Down-Select Results

Series of standardized screening tests we developed to evaluate new catalysts. During down-select process four catalyst systems from three subcontractors including USC, NEU and UTC FC were subjected to liquid cell tests and fuel cell performance measurements as a part of down-select process. Commercial carbon supported pure Pt was used as a baseline catalyst. Ex-situ electrochemical areas (ECAs), oxygen redox reaction (ORR) activities, measured using rotating disk electrode (RDE) and fuel cell performance testing were used for screening. UTC FC catalyst systems has shown mass

activity more than twice that of pure Pt catalyst. PtCo that was synthesized in NEU using micellar technique has also shown the activity higher than Pt baseline but lower than that of UTC FC's PtCo. UTC FC catalyst systems have shown mass activity more than twice that of pure Pt catalyst. PtCo that was synthesized in NEU using micellar technique has also shown the activity higher than Pt baseline.

All the catalyst systems were also tested in fuel cells as cathodes in catalyst coated membranes (CCMs). The state-of-art MEAs were fabricated in UTRC using screen-printing method. The fabrication method was tested prior to down-select. It has been shown that UTRC MEAs are comparable to the commercial MEAs, and the performance reproducibility was shown to be excellent. Results of fuel cell performance tests are shown in Figure 21.

In agreement with the RDE experiments PtCo/C and PtIrCo systems synthesized in UTC FC using carbothermal method showed superior performance and were down-selected for CCM optimization in Phase 2. NEU was selected to work on further improvement of their PtCo/C catalyst. Catalyst from USC showed high initial performance but rapidly decayed under fuel cell operating conditions. It should also be noted that even though USC PtNi electrodes show high performance, Pt loadings in these electrodes were an

order of magnitude higher than in the rest of the screened systems.

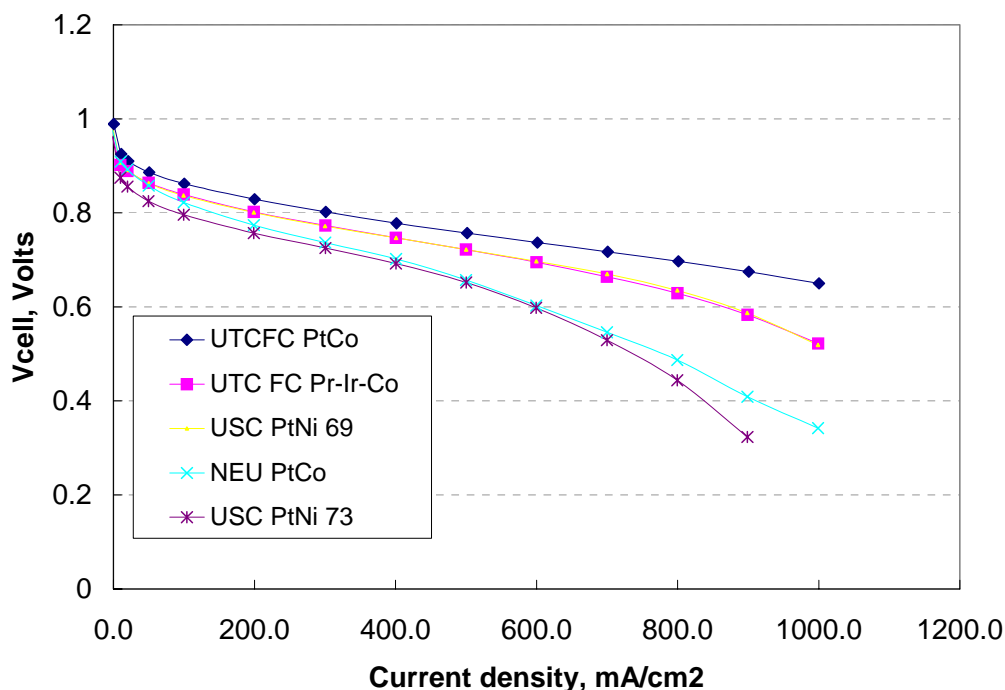


Figure 21. Results of fuel cell performance tests on Pt alloy cathode catalysts. Testing conditions: H₂/Air, 65°C, 1atm. Anode: Pt/C.

In addition to the experimental work, extensive modeling effort was put into the understanding Pt alloys behavior as catalysts for ORR. CWR used a model for reversible potential for the formation of reaction intermediates on electrocatalyst surfaces. It was shown that the Pt-skin on platinum alloyed with chromium or cobalt forms adsorbed hydroxyl at higher potential than on the Pt(111) electrode surface. A correlation is found where the greater the amount of cobalt in the alloy, the greater the increase in the reversible potential. These results correlate with the decrease in overpotential for the four-electron reduction of oxygen that is observed on alloy cathodes relative to non-alloyed Pt electrodes, confirming that OH(ads) is a surface site blocker, causing the overpotential for oxygen reduction. Additional model work shows that in the first reduction step OOH(ads) dissociates easily, forming O(ads) and OH(ads), and the adsorbed oxygen is reduced at a potential that is higher than that for OH(ads) reduction,

which means that on Pt and the Pt-skin OH(ads) is the only surface poisoning intermediate, aside from H₂O(ads).

Phase 2.

PtCo CCM Optimization

PtCo electrodes were optimized for best performance in UTC FC flowfield configuration planform. Among optimize factors were ionomer content in electrode layers, thickness of the anode/cathode and membrane choice. Performance of PtCo/Pt CCM with 0.2mgPt/cm²_0.15mgPt/cm² is shown in Figure 22. Performance of this CCM is compared to the Pt_Pt baseline (total Pt loading = 0.8mg/cm²). Because of increased activity of PtCo catalyst, performance in the kinetic region of polarization curve matches that of Pt CCM of 2x cathode Pt loading. Additional mass transport benefit is obtained in the middle current densities range due to thinner electrodes used. Additional more drastic changes are required to optimize for high current densities (>1A/cm²) where the flooding typical for alloy electrodes is observed.

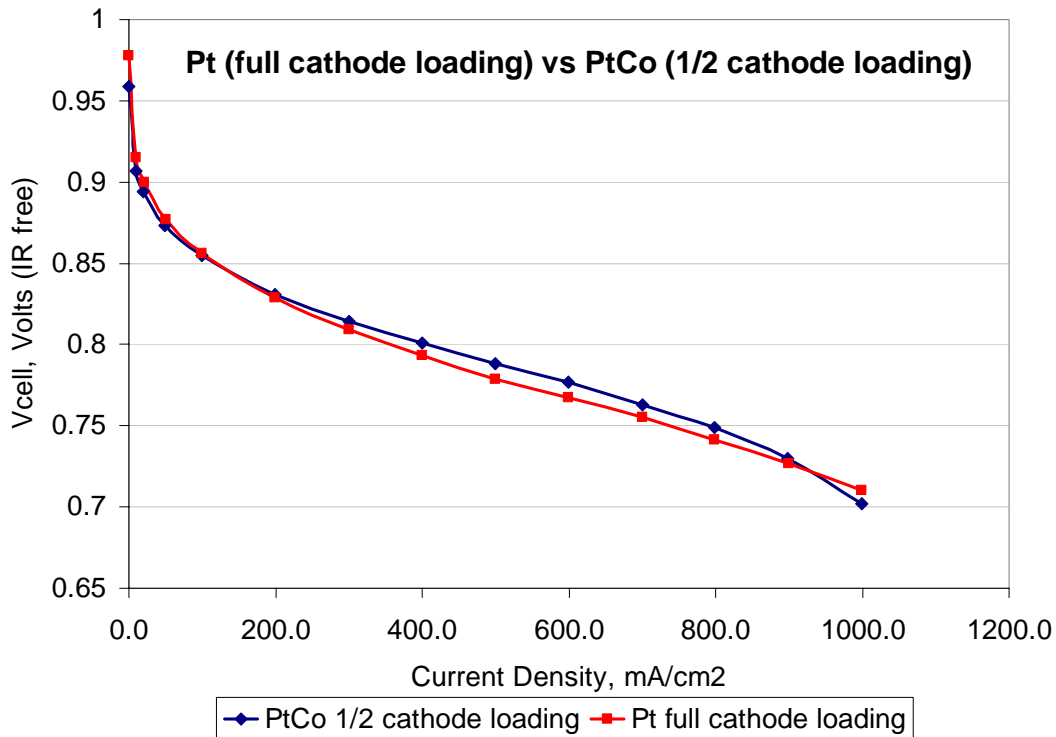


Figure 22. Full size single cell performance of PtCo_Pt and Pt_Pt MEAs. Test conditions: 65°C, H₂/Air, 101kPa (abs).

Alloy Durability

Fuel cells with Pt, PtCo, PtFe and PtIrCo used as cathode catalyst were subjected to potential cycling in the range of high voltages where Pt dissolution is expected to take place. Alloy durability was investigated in cyclic tests at 65°C and 120°C. The cells were subjected to potential cycling between 0.87 V and 1.2 V vs RHE using a potential square wave profile. Cell was held at each potential for 30 sec. The H₂/O₂, H₂/Air performance, and ECA of the CCMs were periodically evaluated every 400 cycles. Summary of ECA loss during these tests is shown in Figure 23. As can be seen from the chart, PtIrCo demonstrated 5x electrode stability improvement compared to pure Pt.

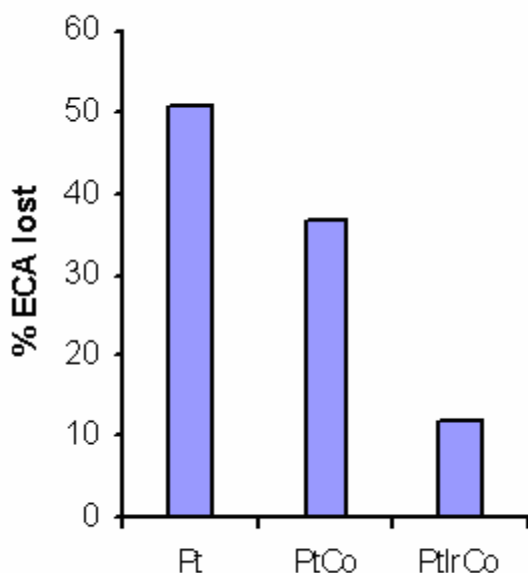


Figure 23. ECA loss during cyclic durability test at 65°C.

Similar cell compositions were subjected to high temperature cathode potential cycling. Upper voltage during cycling was lowered to 1.05V to minimize alloy dissolution data contamination from carbon corrosion effect. Test temperature was 120°C. ECA loss results for Pt, PtIrCo and PtCo catalysts are shown in Figure 24. Pt cells showed severe performance degradation with about 50% ECA loss after 2200 cycles. PtIrCo cell showed

very little degradation during the same cycling time. Figure 25 shows corresponding performance curves from Pt and PtIrCo electrodes before and after cycling.

Effect of carbon support was also investigated. Two cells were run with PtCo on Vulcan and KetjenBlack used as catalyst support. PtCo/Vulcan cell showed very little decay for about 1000 cycles. Average degradation rate after 1000 cycles was similar to PtCo/KetjenBlack cell.

Figure 26 shows results of EMPA test that was done as a part of post test after potential cycling. These results show no Ir or Co and reduced Pt in the membrane when PtCo and PtIrCo alloys are used as cathodes. This suggests that the use of these catalysts would also minimize membrane poisoning that may occur during cycling.

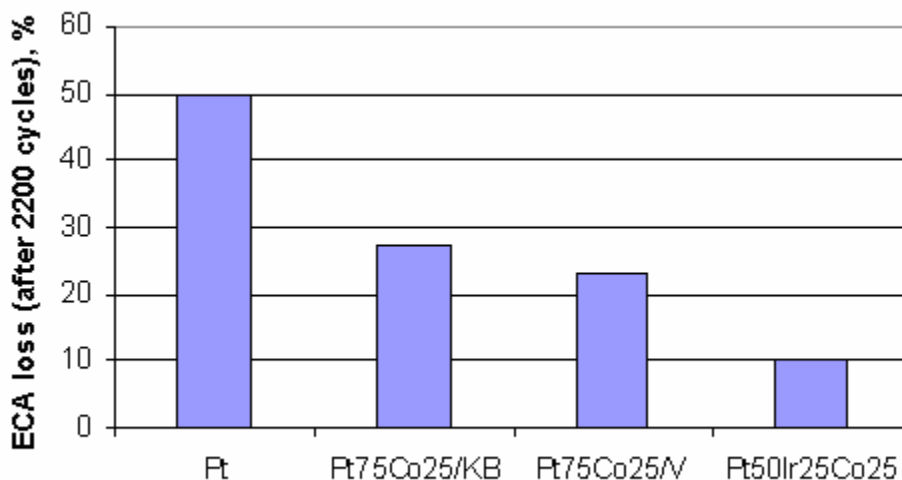


Figure 24. Cathode ECA loss during high temperature potential cycling using different alloys. Data points represent ECAs after 2200 cycles.

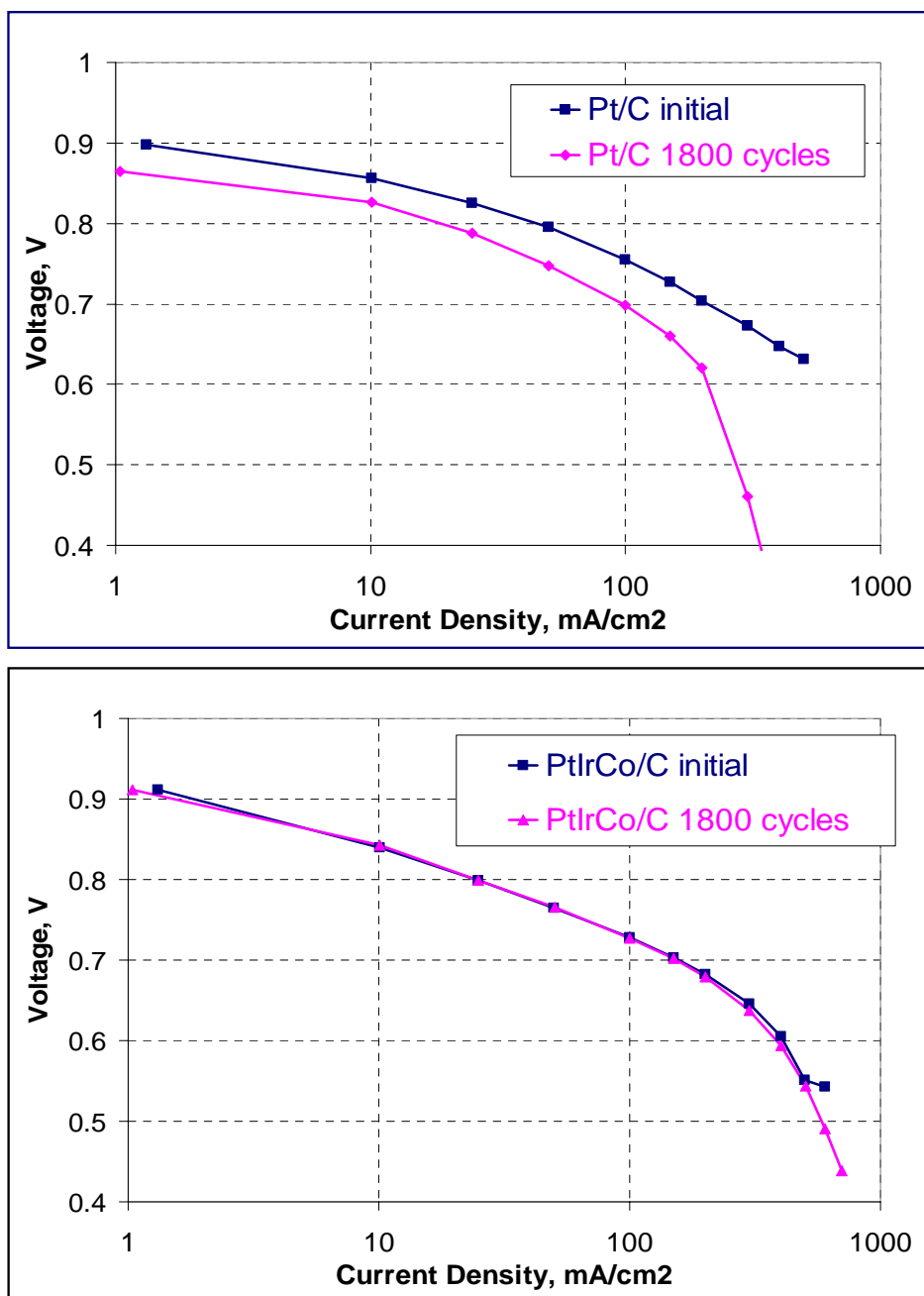


Figure 25. Pt and PtIrCo fuel cell performance curves (H_2/O_2) before and after potential cycling tests.

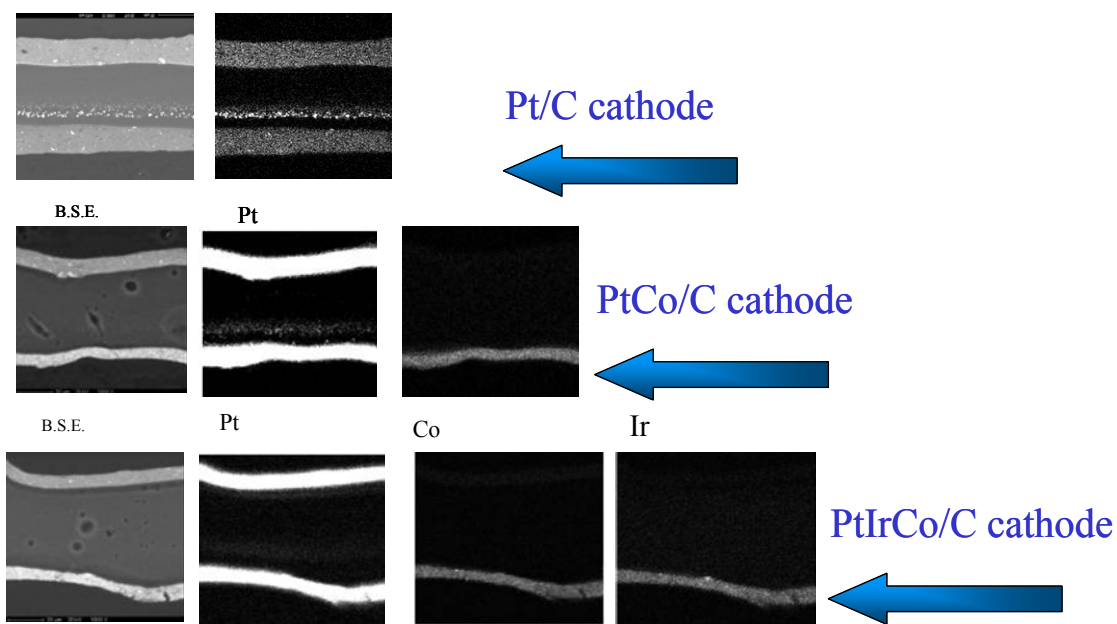


Figure 26. EMPA results of MEAs after potential cycling tests.

Phase 3.

PtCo 20-cell stack demonstration

20-cell advanced cathode catalyst stack for demonstration of PtCo cathode performance was built and acceptance test was run in UTC FC. PtCo MEAs had a total loading of $0.35\text{mgPt}/\text{cm}^2$ per cell with $0.2\text{mgPt}/\text{cm}^2$ each cathode. The stack was run at 65°C coolant inlet temperature. Acceptance test included resistance measurements, sensitivity to pressure changes, polarization curves on H_2/Air . Summary of the test results is shown in Figure 27 and Figure 28.

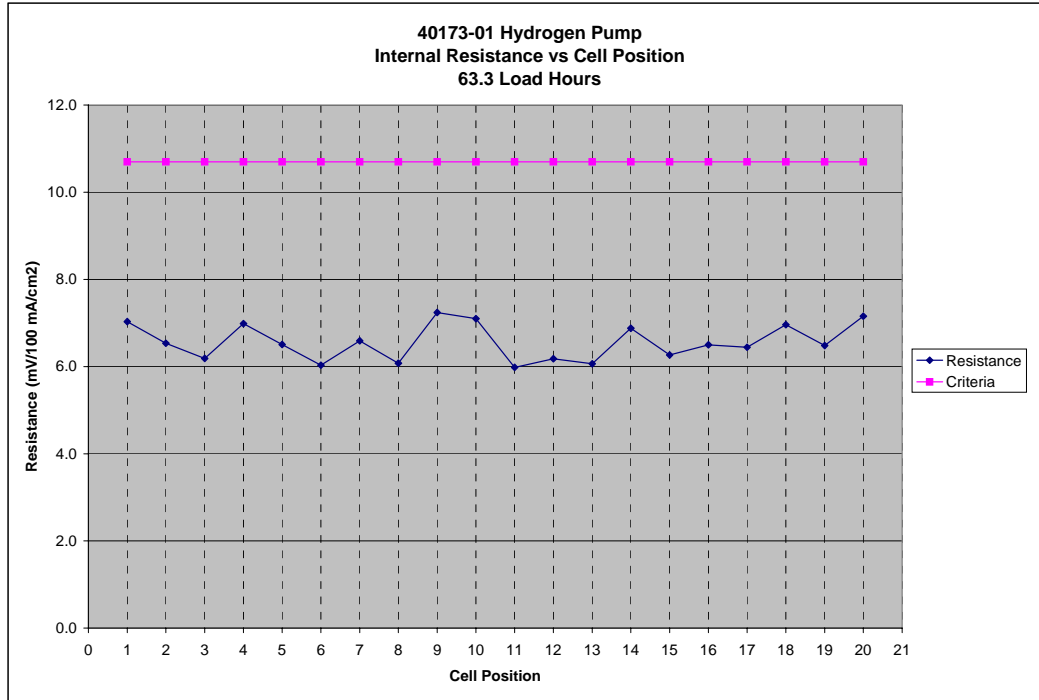


Figure 27. Average Cell Electrical Resistances during Hydrogen Pump on PtCo 20-cell stack

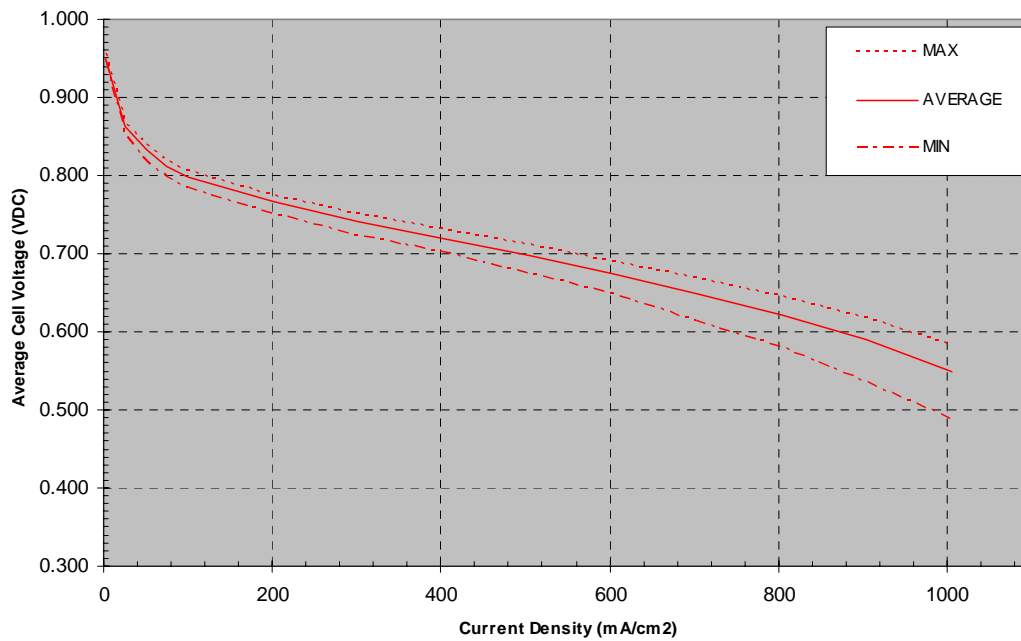


Figure 28. Average PtCo MEA Cell Voltage during Load Calibration on H₂/Air at 80/40% Utilizations

After the acceptance tests the stack was delivered to ANL for durability studies.